



Article

Optimization and mechanisms analysis of indigo dye removal using continuous electrocoagulation

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ABSTRACT

Electrocoagulation (EC) is among the most effective techniques that remove color and decontaminate effluent. Coagulants are delivered *in situ* by anode corrosion. In this research, indigo dye removal using iron electrodes in continuous electrocoagulation process and the responsible species for decolorization were investigated. The Response Surface Methodology (RSM) was used to optimize the process parameters. The finding in this study shows that at fixed conductivity at $15,000 \mu\text{S} \cdot \text{cm}^{-1}$, the neutral conditions (pH from 6 to 8), the low absorbance, the low flow rate and the high voltage level enhance the color removal efficiency. The high R^2 value of 97.8% and ANOVA analyses show a good correlation between the experimental and predicted results. Under the optimum conditions, which are pH of 7.5, solution concentration of $60 \text{ mg} \cdot \text{L}^{-1}$, inlet flow rate of $2 \text{ L} \cdot \text{min}^{-1}$ and voltage of 47 V, the predicted decolorization of 94.083% was achieved at 93.972% with a total cost of $0.0927 \text{ USD} \cdot \text{m}^{-3}$ of treated effluent. At the optimum pH (7.5), the zeta potential value (-4 mV) of the effluent during EC match with the one of iron III hydroxide. The dye removal is ensured thanks to physical adsorption and flocculation. The results exposed in this work prove that the continuous electrocoagulation process could be successfully used for indigo dye removal at industrial scale.

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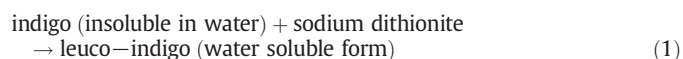
1. Introduction

The textile and clothing sector is very important for the Tunisian economy with more than 1800 industrial enterprises and Jean pants are the most exported product [1]. But one only pant consumes about 100 L of water for dyeing and finishing and the most used dye for jeans is the blue indigo.

Indigo is historically the purplish blue color extracted from the leaves and stems of indigotier [2]. It's evident that indigo has already been used in mummy cloths in ancient Egypt [3]. However, before the synthetic dyes were developed in the 19th century, indigo and other dyes were extracted from plants [4].

The indigo dye belongs to the class of vat dye, which means that it needs to be reduced to its water soluble form known as leuco-indigo with pale yellow color before dying. When the reduced leuco form is absorbed into the fibers, it will be oxidized back by oxygen and returned to the insoluble form in the fiber [5]. There are several techniques for the reduction of indigo, the oldest one is based on microbial fermentation in a vat that contains the indigo dye and other nutriment to ensure bacterial proliferation [6]. Recently, many researches were conducted to find novel reducing processes for the indigo reduction such as electrochemical reduction, glucose also has been known to be a reducing agent for

indigo, but results are unsatisfactory and this process needs high temperatures and strong alkaline conditions [7]. Actually most of dyes use sodium dithionite or hydrosulfite with chemical formula $\text{Na}_2\text{S}_2\text{O}_4$ to facilitate their production [8]. Eq. (1) shows the reduction reaction of indigo to its soluble form.



To resolve dyeing and finishing problems and to limit the contamination, several researches and many techniques have been published in literature but with much limitation. The biological technique alone is not very efficient [9] because of the low biodegradability of chemical products and dyes used in the dying process. Moreover, it needs long treatment time, large land, high energy consumption and frequent maintenance [10]. Concerning the physicochemical process such as adsorption technique [11,12], coagulation-flocculation and advanced oxidation process [13–15] they are quite effective for the decolonization of textile effluent and for pollutants removal, but also they have many disadvantages such as: high associated chemicals products, complex sludge generated, high cost for adsorbent regeneration, etc. [16,17]. As for, filtration treatment techniques, they are very effective [18,19], however their initial installation and maintenance are very costly [20] and a new waste highly loaded with insoluble dye (indigo) is generated.

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Recently, electrocoagulation (EC) has been applied successfully to treat textile dyes. In fact, this technique has several advantages compared to the other conventional treatment techniques, since it uses low cost equipment and generates a low amount of sludge. The coagulant is produced *in situ* by the sacrificial anode, and thus there are no additional chemical products in all the process [21]. Moreover, the sludge generated could be easily dewatered by several techniques [22].

The applied potential between electrodes generates the coagulant species from scarified electrodes dissolution, in the same time hydrogen is simultaneously developed at the cathode and carries the flocculated contaminants to the surface of the treated solution. Coagulant species (metal ions, metal polymers, metal monomers...) engender the aggregation of the suspended particles and then the adsorption and precipitation of contaminants. In literature, different electrodes have been reported but iron and aluminum are the most efficient and successful for effluent decontamination with low prices.

The EC process could be summarized by anode oxidation and formation of coagulants, the destabilization of the contaminants and breaking of emulsions and finally the formation and sedimentation of the heavy flocs and flotation of light flocculated flocs.

A large number of studies have been published on the textile effluent treatment using electrocoagulation [23–29]. Nevertheless, only very limited information about indigo dye removal have been published [30–32]. Moreover, we noted the absence of an explicit study on the species and mechanisms responsible for the adsorption of dyes. Considering this lack of information, and the high volume of the discharged effluent loaded with indigo dye in Tunisia, the preset paper aims to test and evaluate a new method, more effective, less expensive and very compact at industrial scale based on electrochemical techniques, especially the electrocoagulation (EC) in continuous process without effluent recirculation using iron electrodes. Thus, in the first place, the effects of the main operating parameters like conductivity, pH, initial concentration, initial flow rate and voltage on the dye removal were investigated in details. Optimum conditions are also defined in this study, which will be very useful for the designing and the adjustment of industrial station based on EC to treat a real textile effluent. Second we establish which iron hydroxides, formed during EC, are responsible of the blue indigo removal by recognition of the zeta potential of the effluent at different circumstances and in which step of EC the color was removed.

2. Materials and Methods

2.1. Synthetic wastewater and chemicals

The stock solution was prepared by dissolving the Blue Indigo dye (CI Vat Blue 1: BEZEMA AG, Switzerland), obtained from local company into deionized water, then this solution was diluted to the desired concentration. In tanks with total volume of 10 L was mixed: 100 g of pure powdered indigo and 200 g of sodium dithionite (Fluka, Germany) with deionized water at 80 °C to enhance the reducing process. The dyeing solution was prepared in a similar ratio as prepared by the industrial company. Before dyeing, this solution has to be diluted more than 200% in the dyeing plant. Table 1 summarizes the main characteristics of the indigo dye.

The solution was stored in opaque tank at 4 °C. Except indigo dyes, the other reagents were of analytical grade and were used without additional purification. The pH and conductivity were adjusted by adding hydrochloric acid (HCl 1 mol·L⁻¹; Scharlau) or sodium hydroxide (NaOH 1 mol·L⁻¹; fluka) and sodium chloride (NaCl Sigma-Aldrich).

After identification of the optimum conductivity, this value was adjusted to 15,000 µS·cm⁻¹ for all experiences. The discharge limits (Tunisian standard) are: color 70 Pt-Co (The Platinum-Cobalt color scale), pH of 6.5–8.5, COD (Chemical Oxygen Demand) 90 mg·L⁻¹, and BOD₅ (Biological oxygen demand) 30 mg·L⁻¹.

2.2. Analytical measurements

The dye concentration was estimated from its absorbance at the maximum wavelength $\lambda_{\max}$ of 620 nm using HACH LANGE DR3900 UV-Vis spectrophotometer (200–800 nm). For this reason, a calibration plot based on Beer–Lambert's law was established by relating the absorbance to the concentration. Since the spectrophotometers have a maximum absorbance for a value of 2.5 and the linear function between concentration and absorbance is valid only at low concentration values where the Beer Lambert law is fulfilled, all concentrations that exceed 35 mg·L⁻¹ were diluted prior to spectrophotometry analysis. Moreover, the effect of the pH on the wavelength $\lambda_{\max}$ was investigated and this value did not change when the pH change.

The pH of the solutions was measured using a HANNA INSTRUMENT HI 2202 pH meter, whereas conductivity, electric intensity and zeta potential were measured respectively using a conductivity meter HANNA instruments HI8819, multi-parameter analyzer METRIX PX110 - Digital TRMS and a zeta-meter 3000, Malvern Instruments.

All samples were previously centrifuged at 4000 r·min⁻¹ for 10 min to remove the flocs, and limpid supernatant liquid were collected and filtered to ensure the solutions were free from residual flocs before the determination of the absorbance. The zeta potential is measured after a rest time of 30 min in the second reactor dedicated to sedimentation.

The color removal efficiency (*Re* %) of the synthetic wastewater was calculated from concentration change and defined by Eq. (2).

$$Re = 100\% \times (C_i - C_f) / C_i \quad (2)$$

C_i and C_f are the initial and final absorbance in the inlet and the exit streams of the continuous EC reactor, respectively.

2.3. Experimental setup and procedure

As it could be seen in Fig. 1, the continuous EC pilot is composed from a trapezoidal polyethylene reactor with a rectangular column of 2.4 L. This pilot contains two chambers, the first one for inlet effluent and reaction process, it contains a set of 30 iron parallel electrodes totally emerged and allowing an effective volume of 2 L and a 2877.49 cm² electrodes surface area. The electrodes (length = 15.8 cm, width = 6.28 cm, thickness = 1.6 mm) are fixed on a plastic electrodes guide with a constant gap between the two neighboring of 4 mm. The two power blades are placed at opposite ends of electrodes guide and they are connected to a panel control allowing an alternating current power, which supplies a range from 0 to 220 V. The second chamber was designed for the solid and flocs settling. The floated sludge was continuously removed from the second chamber by overflow.

The bipolar mode and the vertical parallel connection were used in view of its simple setup and less maintenance cost during operation. Typically, polyvalent metal electrodes such as iron or aluminum are used to benefit from the coagulating properties of multivalent ions [33]. Nevertheless, in our study we chose iron for it is cheaper.

The flow rate was adjusted with variable frequency pump and current was modified by control panel suppliers. The synthetic wastewater

Table 1
Main characteristics of Blue indigo dye

Color index number	CAS number	FORMULA	Molecular weight	Melting point	UV absorption $\lambda_{\max}$ (leuco-indigo)
CI Vat Blue 1	482-89-3	C ₁₆ H ₁₀ N ₂ O ₂	226.26	390–392 °C	620 nm

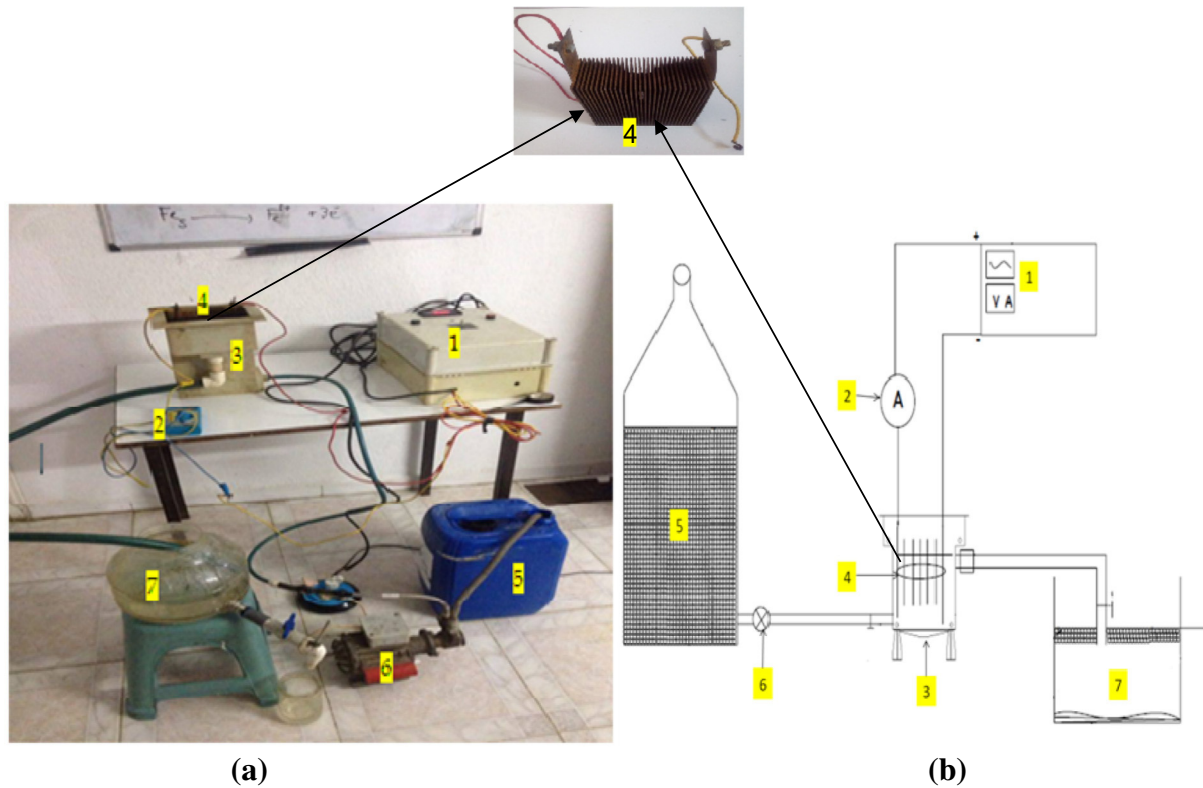


Fig. 1. (a) Real experimental continuous EC pilot, (b) schematic continuous EC process. 1: control panel of current supplier, 2: ammeter, 3: EC reactor, 4: iron electrodes, 5: tank with untreated effluent, 6: variable frequency drive pump, 7: second chamber for flocs and solid settling.

was fitted from the bottom of reactor and treated wastewater was collected from the top of the second chamber. After each run, electrodes were cleaned with wire brush, dipped in diluted HCl solution then washed with deionized water.

2.4. Process optimization using Response Surface Methodology (RSM) approach

In this study, the standard RSM design called Central Composite Design (CCD) was applied to perform and to model the responses of continuous EC process. From literature [34,35], the CCD design is a statistical method which uses experimental data to predict output variables named response (Y) by identifying a correlation between input variables named factors (X) involving their interactions. This statistical CCD method is appropriate for fitting a quadratic surface and for the identification of the best-input value to optimize the process with minimum of experiments [36].

Eq. (3) determines the number of required experiments when CCD design was applied.

$$N = 2^n + 2n + n_0 \quad (3)$$

N is the number of experimental runs, n the number of factors and n_0 the central runs used to evaluate the experimental error. As it could be seen in Table 2, in the present study, 4 factors (solution pH, solution absorbance, inlet flow rate and voltage) at five levels (-2 , -1 , 0 , 1 and $+2$) were considered. The low and high levels are fixed on basis of literature [29] and preliminary experiments. To analyze the relationship between the response and the factors, the second order polynomial equation was fitted according to Eq. (4) and then the performance of the system was evaluated.

$$Y = \beta_0 + \sum_{i=1}^n \beta_i X_i + \sum_{i=1}^n \beta_{ii} X_i^2 + \sum_{i=1}^n \sum_{j=i+1}^n \beta_{ij} X_{ij} \quad (4)$$

2.5. Operating cost

For EC process, the operating cost includes cost of energy, electrodes, chemicals, sludge disposal and maintenance. In this work, to evaluate the total operating cost (TC) of indigo dye removal using EC process, only the two most important costs which are electrical energy cost (EnC) and electrodes consumption cost (EIC) are considered. Other costs such as maintenance, chemical consumption and sludge treatment were neglected. According to the commonly used Eqs. (5) to (7) [37,38] the total cost could be calculated as follow:

$$EnC = U \times I \times t = \frac{U \times I \times t}{V} (\text{kW} \cdot \text{h} \cdot \text{m}^{-3}) \quad (5)$$

$$EIC = \frac{I \times Mw \times t}{n \times F \times V} (\text{kg Fe} \cdot \text{m}^{-3}) \quad (6)$$

$$TC = \alpha EnC + \beta EIC (\text{USD}) \quad (7)$$

U is the applied voltage (kV), I is the current (A), t is the EC time (h) and V is the treated volume (m^3), n is the number of transferred electrons, Mw is the molecular mass of iron and F is the faraday constant.

Table 2
Factors and levels of experimental design for continuous EC process

Factors	Levels				
	-2	-1	0	1	2
X1, initial pH	2,5	5	7,5	10	12,5
X2, initial concentration/ $\text{mg} \cdot \text{L}^{-1}$	10	35	60	85	110
or Initial absorbance (au) at $\lambda_{\text{max}} = 620 \text{ nm}$	0.423	1431	2439	3.447	4.455
X3, flow rate/ $\text{L} \cdot \text{min}^{-1}$	1	1,5	2	2,5	3
X4, voltage/V	5	20	35	50	65

In December 2017 the cost of 1 kW·h (α) was 0.117USD and the cost of 1 kg plate iron (β) was 0.72 USD.

$$TC = 0.117 \text{ EnC} + 0.72 \text{ EIC} = 0.0927 \text{ (USD} \cdot \text{m}^{-3}\text{)}$$

3. Results and Discussion

3.1. Optimum conductivity

The influence of the conductivity of the synthetic effluent has been studied by the addition of sodium chloride to the prepared solution. This parameter controls the resistance of the polluted water and subsequently the current intensity (I) passing through the effluent at a constant voltage [39,40]. The consumed energy during the EC process is proportional to both applied voltage between the electrodes and the current intensity passing through the wastewater. An increase in conductivity implies a low resistance and subsequently a low energy consumption. However, an excessive concentration of NaCl in the effluent leads to the formation of passive layers, which reduce the process efficiency. The analysis of the indigo dye removal at various conductivities (Fig. 2) and at $2 \text{ L} \cdot \text{min}^{-1}$ flow rate (1 min residence time) shows a slight increase in decolorization when starting at low conductivity, but this increase becomes insignificant at a conductivity over than $2000 \mu\text{S} \cdot \text{cm}^{-1}$, then a significant decrease was suddenly observed when the conductivity value exceeded $15,000 \mu\text{S} \cdot \text{cm}^{-1}$. This result is in good harmony with those reported by Bayramoglu *et al.* [41] who confirms that the conductivity has no significant effect on the EC. However, Daneshvar *et al.* [39], states that the increase in conductivity leads to improve the color and the COD removal when treating effluent loaded with basic dyes, which behaves differently from indigo dye, assimilated to an acid dye, in its soluble form. Also, in previous study [42], Ahmadzadeh, S., & Dolatabadi, M. confirm that using KCl salt as electrolyte gives better pollutants removal efficiency than using NaCl. Furthermore, Majid Rezayi.

et al. [43] used this parameter to investigate the stability of some complexes in water.

3.2. Evaluation of experimental results with CCD

In this work, the conductivity was fixed at $15000 \mu\text{S} \cdot \text{cm}^{-1}$. However, the four considered factors (variables) for the CCD design were pH, concentration C ($\text{mg} \cdot \text{L}^{-1}$) or Abs (au), flow rate ($\text{L} \cdot \text{min}^{-1}$) and voltage (V). The response which is the indigo dye removal efficiency Re (%) was developed in Table 3 with a CCD matrix including experimental and predicted data.

To describe the model, the full quadratic regression model for indigo dye removal ($Y = Re$ (%)) in terms of uncoded parameters was developed as following Eq. (8).

$$\begin{aligned} Y = Re = & -4.9362 + 11.5226 \text{ pH} + 13.06 \text{ Abs} + \\ & 35.0172 \text{ Flow rate} + 0.9766 \text{ Voltage} - 0.5033 \text{ pH} \times \\ & \text{pH} - 2.917 \text{ Abs} \times \text{Abs} - 5.5827 \text{ Flow rate} \times \\ & \text{Flow rate} - 0.0084 \text{ Voltage} \times \text{Voltage} - 0.172 \text{ pH} \times \\ & \text{Abs} - 2.3860 \text{ pH} \times \text{Flow rate} - 0.0194 \text{ pH} \times \\ & \text{Voltage} - 0.2059 \text{ Abs} \times \text{Flow rate} + 0.0352 \text{ Abs} \times \\ & \text{Voltage} - 0.0622 \text{ Flow rate} \times \text{Voltage} \end{aligned} \quad (8)$$

The significance of each parameter and their interaction was evaluated by applying P -value. At 95% confidence level, to be significant, the P -value should be less than 0.05 [44]. The amounts P ($P = 0$) of all parameters and their square means that the 4 factors are significant for indigo dye removal. Nevertheless, P values ($P \geq 0.05$) for all interaction parameters except the interaction $\text{pH} \times \text{Flow rate}$ means that the other five interactions between parameters are insignificant for the response.

After removing insignificant coefficients, the developed quadratic regression model could be simplified to Eq. (9)

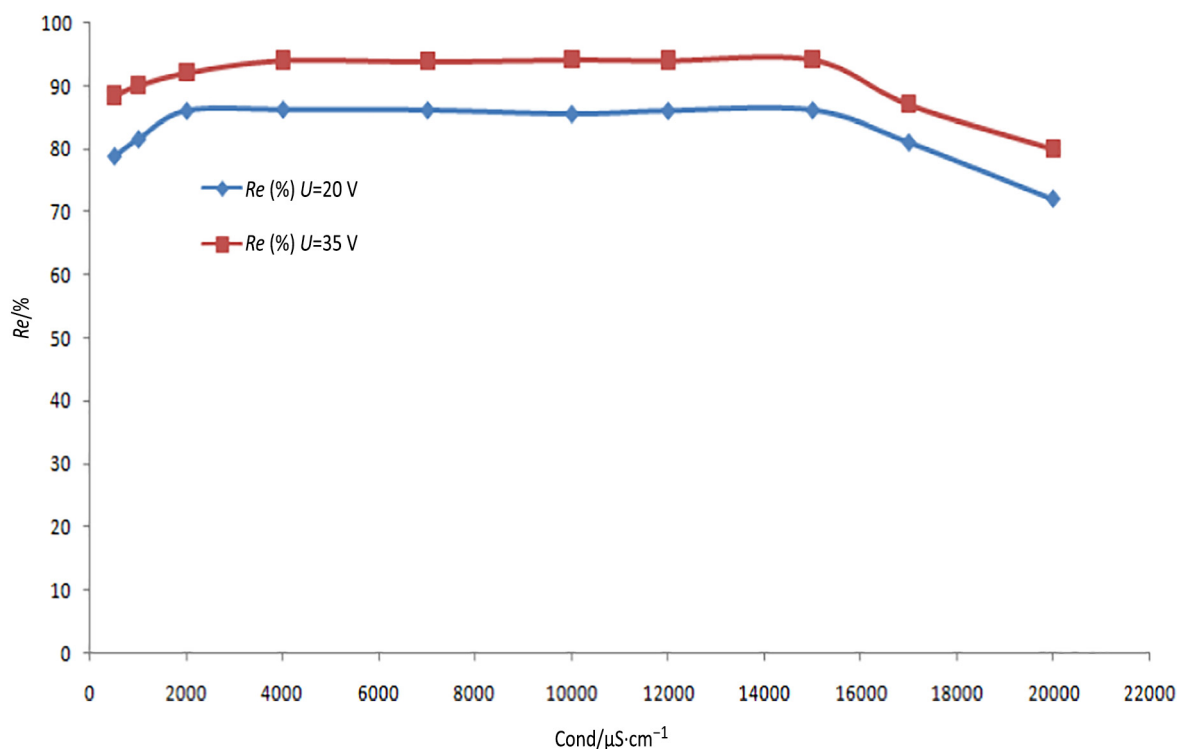


Fig. 2. Evolution of the decolorization (Re %) with the conductivity at different voltage (pH = 7.5 concentration $C = 60 \text{ mg} \cdot \text{L}^{-1}$, Flow rate = $2 \text{ L} \cdot \text{min}^{-1}$ (1 min residence time)), mean error = 0.2%.

Table 3

CCD matrix including experimental and predicted color removal efficiency for synthetic effluent

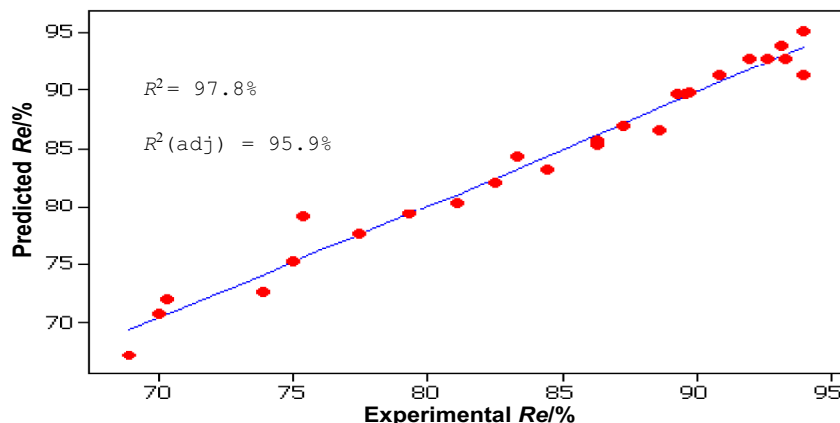
Run	X1	X2	X3	X4	pH	Abs (a u)	Flow rate/L·min ⁻¹	Voltage/V	Experimental Re/%	Predicted Re/%
1	−1	−1	−1	−1	5	1.431	1.5	20	88.64	86.57
2	1	−1	−1	−1	10	1.431	1.5	20	86.36	85.37
3	−1	1	−1	−1	5	3.447	1.5	20	84.43	83.27
4	1	1	−1	−1	10	3.447	1.5	20	81.13	80.34
5	−1	−1	1	−1	5	1.431	2.5	20	86.36	85.79
6	1	−1	1	−1	10	1.431	2.5	20	73.86	72.66
7	−1	1	1	−1	5	3.447	2.5	20	82.55	82.07
8	1	1	1	−1	10	3.447	2.5	20	68.87	67.21
9	−1	−1	−1	1	5	1.431	1.5	50	93.18	93.98
10	1	−1	−1	1	10	1.431	1.5	50	89.77	89.88
11	−1	1	−1	1	5	3.447	1.5	50	91.98	92.81
12	1	1	−1	1	10	3.447	1.5	50	87.26	86.98
13	−1	−1	1	1	5	1.431	2.5	50	90.91	91.34
14	1	−1	1	1	10	1.431	2.5	50	75	75.30
15	−1	1	1	1	5	3.447	2.5	50	89.62	89.75
16	1	1	1	1	10	3.447	2.5	50	70.28	71.98
17	−2	0	0	0	2.5	2.439	2	35	89.33	89.76
18	2	0	0	0	12.5	2.439	2	35	70	70.79
19	0	−2	0	0	7.5	0.423	2	35	83.33	84.31
20	0	2	0	0	7.5	4.455	2	35	77.45	77.69
21	0	0	−2	0	7.5	2.439	1	35	94	95.16
22	0	0	2	0	7.5	2.439	3	35	79.33	79.39
23	0	0	0	−2	7.5	2.439	2	5	75.33	79.18
24	0	0	0	2	7.5	2.439	2	65	94	91.37
25	0	0	0	0	7.5	2.439	2	35	92.67	92.86
26	0	0	0	0	7.5	2.439	2	35	92.67	92.86
27	0	0	0	0	7.5	2.439	2	35	93.33	92.86
28	0	0	0	0	7.5	2.439	2	35	93.33	92.86
29	0	0	0	0	7.5	2.439	2	35	92.67	92.86
30	0	0	0	0	7.5	2.439	2	35	92.67	92.86
31	0	0	0	0	7.5	2.439	2	35	92.67	92.86

$$Y = Re = 11.5226 \text{ pH} + 13.06 \text{ Abs} + 35.0172 \text{ Flow rate} + 0.9766 \text{ Voltage} - 0.5033 \text{ pH} \times \text{pH} - 2.917 \text{ Abs} \times \text{Abs} - 5.5827 \text{ Flow rate} \times \text{Flow rate} - 0.0084 \text{ Voltage} \times \text{Voltage} - 2.3860 \text{ pH} \times \text{Flow rate} \quad (9)$$

The accuracy and quality of the model was evaluated by analyzing the correlation coefficient value R^2 , P -value, the total sum of square and sum square of the residual value. Moreover, the plot of predicted and experimental data for indigo dye removal in Fig. 3 confirms a good agreement between experimental and predicted values. Also, the higher values of R^2 and adjusted R^2 i.e. 97.8% and 95.9% respectively and their good harmony prove the reliability of the model.

To perform the interpretation, the significance and the adequacy of the model were determined by the analysis of variance (ANOVA) [45]. The sum of square of the residual error is insignificant and very low compared to the total sum square of the model ($42.18 < < 1952.67$). Moreover, the P value = 0 for the model and all regressions, so the full quadric regression model developed by RSM is highly significant and can navigate very well the design space. Subsequently, it is very adequate to predict the continuous EC process at any point of the defined space.

Finally the data point of the normal probability plot (figure not shown) of the residuals which forms a straight line and the residuals shows no increasing or decreasing point or predominance of positive or negative residuals, which confirm further that the RSM model is adequate to describe the indigo dye removal efficiency.

**Fig. 3.** Predicted vs experimental values for indigo dye removal Re.

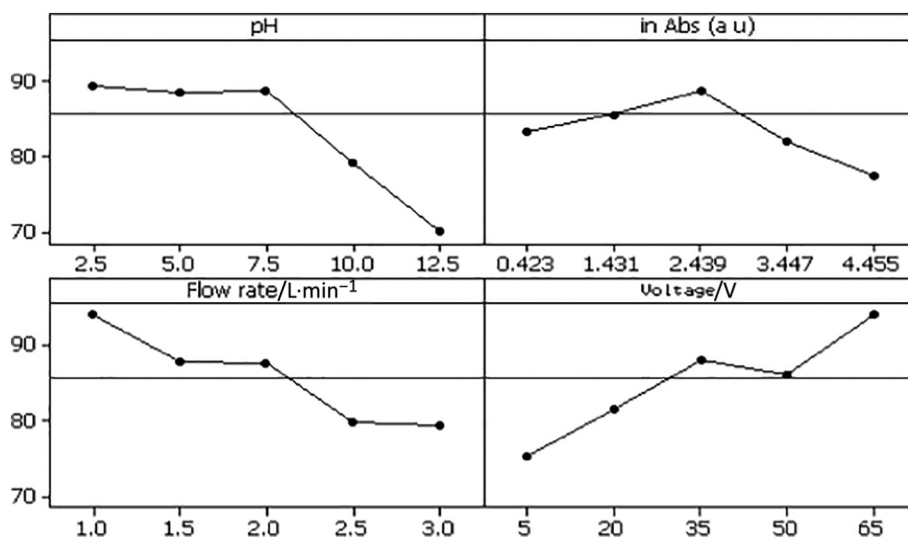


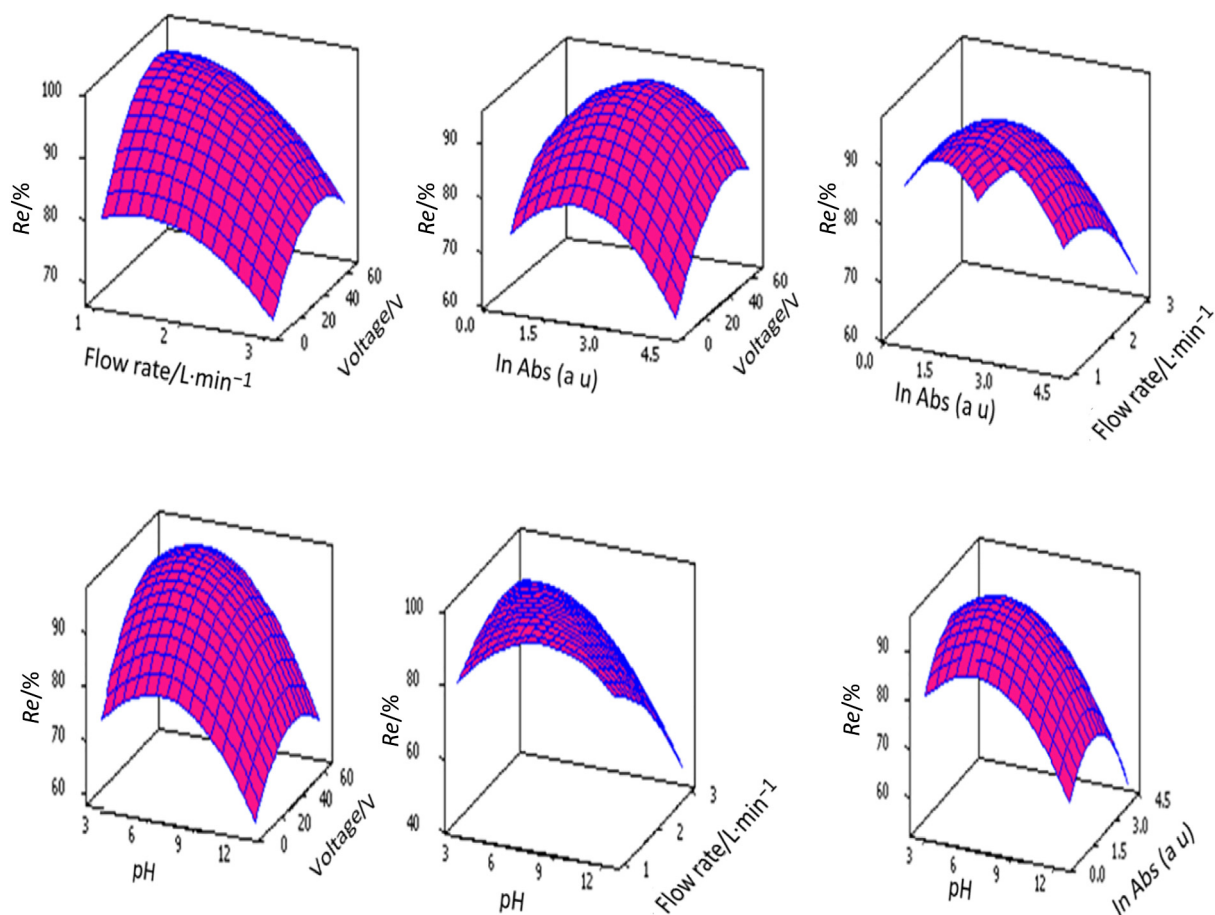
Fig. 4. Main plot for Re (%).

3.3. Effects of operating parameters

The main effects of different parameters on the indigo dye removal efficiency have been illustrated in Fig. 4 given below. 3D graphs have been also provided in Fig. 5 for more clarity and better interpretation of parameters influence.

3.3.1. Initial pH

The initial pH influences directly the electrocoagulation process efficiency [46]. As it could be seen in Figs. 4 and 5, the indigo dye removal efficiency is more important at acidic medium than in basic medium. When the pH increases from 2.5 to 7.5 and then to 12.5 at a constant concentration of $60 \text{ mg} \cdot \text{L}^{-1}$, $2 \text{ L} \cdot \text{min}^{-1}$ flow rate and 35 V, the color removal

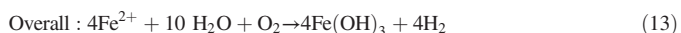
Fig. 5. 3D plots for Re (%) at hold values of pH = 7.5, Abs = 2.439, flow rate = $2 \text{ L} \cdot \text{min}^{-1}$ and 35 V.

efficiency increases from 89.33% to 93.3% and then decreases to reach 70%. From Fig. 5, the 3D plot shows that the high removal efficiency of indigo was obtained in neutral conditions (pH from 6 to 8). When the pH exceeds 9 the process yield decreases owing to the formation of ineffective iron hydroxides species for dye coagulation and the formation of layer on the anode, reducing the iron dissolution [47].

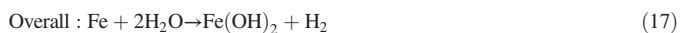
In fact the Fe^{2+} ions are produced in EC reactor by anode dissolution, these ions are oxidized to Fe^{3+} at acidic solution due to the presence of dissolved oxygen and H^+ ions become more prevalent and are reduced to H_2 at the cathode. At the same time, hydroxide ions and oxygen are produced simultaneously in cathodic and anodic regions.

The main reaction occurring during iron EC process can be summarized in Eqs. (10) to (17).

Mechanism 1:



Mechanism 2:



3.3.2. Initial dye concentration

The indigo removal using continuous EC process gave satisfactory results for all tested initial dye concentration, as color removal Re (%) was always higher than 77%. Moreover, as illustrated in Fig. 4, at constant: pH 7.5, $2 \text{ L} \cdot \text{min}^{-1}$ flow rate and 35 V the indigo dye removal efficiency increase from 83.33% to 93.33% when initial concentration increases from $10 \text{ mg} \cdot \text{L}^{-1}$ (0.423 au) to $60 \text{ mg} \cdot \text{L}^{-1}$ (2.439 au). Othmani *et al.* [48] explain this result by the collision theory and thermodynamic limitation, which state that the higher concentration of substance increases the chance of molecules colliding and enhances the reaction speed. However, as it was seen in 3D plot Fig. 5, when initial concentration exceeds $74 \text{ mg} \cdot \text{L}^{-1}$ (3 au), we observe that the more the initial dye concentration increases the more the removal efficiency decreases and the best results were achieved for initial concentration interval of $37 \text{ mg} \cdot \text{L}^{-1}$ to $74 \text{ mg} \cdot \text{L}^{-1}$. Similar results were reported by Gautam *et al.* [47]. This phenomenon may be due to the insufficient number of iron hydroxide complexes released by the electrodes to coagulate the excess indigo dye molecule at higher concentration level [38,48,49].

3.3.3. Initial flow rate

The flow rate is inversely proportional to EC residence time. In other words, a lower flow rate involves a longer residence time, which in turn allows the generated coagulant and the indigo dye molecules to mix correctly and thereby improve the continuous EC process yield. Moreover, as expected by Eq. (6), the longer EC time involved the larger amount of oxidized iron electrodes that mean a large quantity of hydroxide flocks $\text{Fe}(\text{OH})_3$ and $\text{Fe}(\text{OH})_2$, ferric hydroxyls and polymers species, which enhance the removal efficiency and increase the process cost.

As it could be seen in Fig. 4, at fixed pH 7.5, initial concentration of $60 \text{ mg} \cdot \text{L}^{-1}$ and 35 V, the removal efficiency Re (%) decreases from 94% to 79.33% when the initial flow rate increases from $1 \text{ L} \cdot \text{min}^{-1}$ to $3 \text{ L} \cdot \text{min}^{-1}$. Likewise, the 3D plot in Fig. 5 shows that the best removal efficiency was achieved at slower flow rate range. However, decreasing flow rate from $2 \text{ L} \cdot \text{min}^{-1}$ to $1 \text{ L} \cdot \text{min}^{-1}$ did not change significantly the EC yield. It is then advisable to preserve the electrode, reduce the cost and choose the optimum flow rate [32,40,50]. Hammouda and Assadi *et al.* [51,52] explain the effect of flow rate on the pollutant removal efficiencies by the mass transfer between the phases. The efficiencies were enhanced under low flow rate until reaching the equilibrium point where no mass transfer will occur.

3.3.4. Effect of voltage

The current density is among the most important parameters that affect the EC process by controlling the reaction rate [24]. In fact, the quantities of polymers and iron oxide flocks generated from iron electrodes depend, according to Eq. (18), on current density which is in turn proportional to voltage [53]. According to Ohm's law, ($U = R \times I$ (18)), the intensity of current passing through the effluent is closely dependent on the applied voltage between electrodes. The more the applied voltage increases the more the intensity increases, which in turn increases the current density. Therefore, according to Faraday's law, Eq. (6) below, the amount of dissolved iron ions increases which enhances the color removal efficiency.

As reported in Fig. 4, at constant: pH 7.5, $2 \text{ L} \cdot \text{min}^{-1}$ flow rate and concentration of $60 \text{ mg} \cdot \text{L}^{-1}$, the removal rate jumps from 75.3% to 94% when the voltage increases from 5 V to 65 V. Nevertheless, in 3D plot Fig. 5, it is clearly observed that there is no significant improvement in process yield when the voltage exceeds 35 V. This phenomenon could be explained by the reaction saturation, so the most of electrical energy was wasted in heating the effluent [54]. Donneys-Victoria *et al.* [55] found that increasing the current density involves an increase in the pollutants removal efficiency until an optimum value. However, they found also, that the increase of the current density from 50 to $80 \text{ A} \cdot \text{m}^{-2}$ did not progress dye removal yield, and they explained this by the formation of passivating layers on the anodes, which increases the resistances in EC cell at high current densities. Furthermore, Dolatabadi & Ahmadzadeh [56] explain this phenomenon by the oxidation of water and the generation of some inorganic oxidants at high current density, which reduces the removal efficiency of the process. Thus, to avoid higher cost, process maintenance and electrode changing, it would be better to choose the optimum voltage when the efficiency increases slightly by increasing the voltage [48,57,58].

3.4. EC process optimization

One of the most important reasons from using RSM in designing the experiments was to optimize the different parameters of the EC to obtain the maximum response [59]. The desired function of Derringer and Suich of Minitab V.14.0 software was used to determine the optimum parameters values that maximize the desirability function from the developed model by CCD Design Eq. (8). Table 4 summarizes the optimum parameters values along with the total cost and predicted and experimental data of color removal efficiency. The desired target for the response (indigo dye removal efficiency) was chosen to a maximum

Table 4
Optimization of indigo removal efficiency Re (%) (Target 100%)

pH	Absorbance (au)	Flow rate/L·min ⁻¹	Voltage/V	Total cost/USD·m ⁻³	Predicted Re /%	Experimental Re /%
7.5	2.439	2	47	0.0927	94.0834	93.972

value of 100% and the 4 initial parameters of pH, absorbance, flow rate and voltage were selected without starting values. To test the model sufficiency and the conformity of the optimized data, additional experiment was realized under the optimum conditions proposed by Minitab software and collected from the developed model.

Under the optimum conditions, the predicted decolorization of 94.083% was achieved at 93.972% with 0.0927 USD·m⁻³ of treated effluent. The negligible difference of 0.111% between experimental and predicted value, validates the accuracy of the developed model and confirms that the RSM is a powerful tool for the optimization of the continuous EC process parameters.

After treatment, the final effluent color reached was 62 Pt-Co, which confirms that the used method can ensure the Tunisian discharge limits.

3.5. Zeta potential

The stability of the colloidal particles is determined by their physico-chemical properties. In fact, the similar charged colloids repel each other to maintain a stable system. At the same time, counter ions (the positive charged ions) are attracted to the negatively charged particles

to keep the electroneutrality. This attraction forms an electric double layer. A fixed layer called the Stern layer, and an outer layer called diffuse layer which is composed of heterogeneous charges, where the ions move freely due to diffusion. It is difficult to measure the charge at the colloidal surface, due to the charge concentrations in the Stern and diffuse layers. Therefore, the zeta potential is used as an experimental measure of the particle charge when moving through the effluent, which provides a clear idea about the stability of the pollutants [60].

At optimum pH of 7.5, the zeta potential of the synthetic effluent was -27 mV. Many mechanisms are involved in the pollutants removal when using EC process. The zeta potential evolution during EC process versus the pH, the applied voltage and the flow rate was measured and plotted in Fig. 6 (a–c). The obtained data was compared to previous results (Figs. 7 and 8) in order to identify the charges of the different species formed during EC process and to establish which formed species produced during EC, are responsible of decolorization.

It can be observed from Fig. 6 that the zeta potential depends only on the solution pHs since, it remains negative and almost constant at fixed pH of 7.5 under different voltage and different flow rate. However, comparing this figure with previous study we can conclude that:

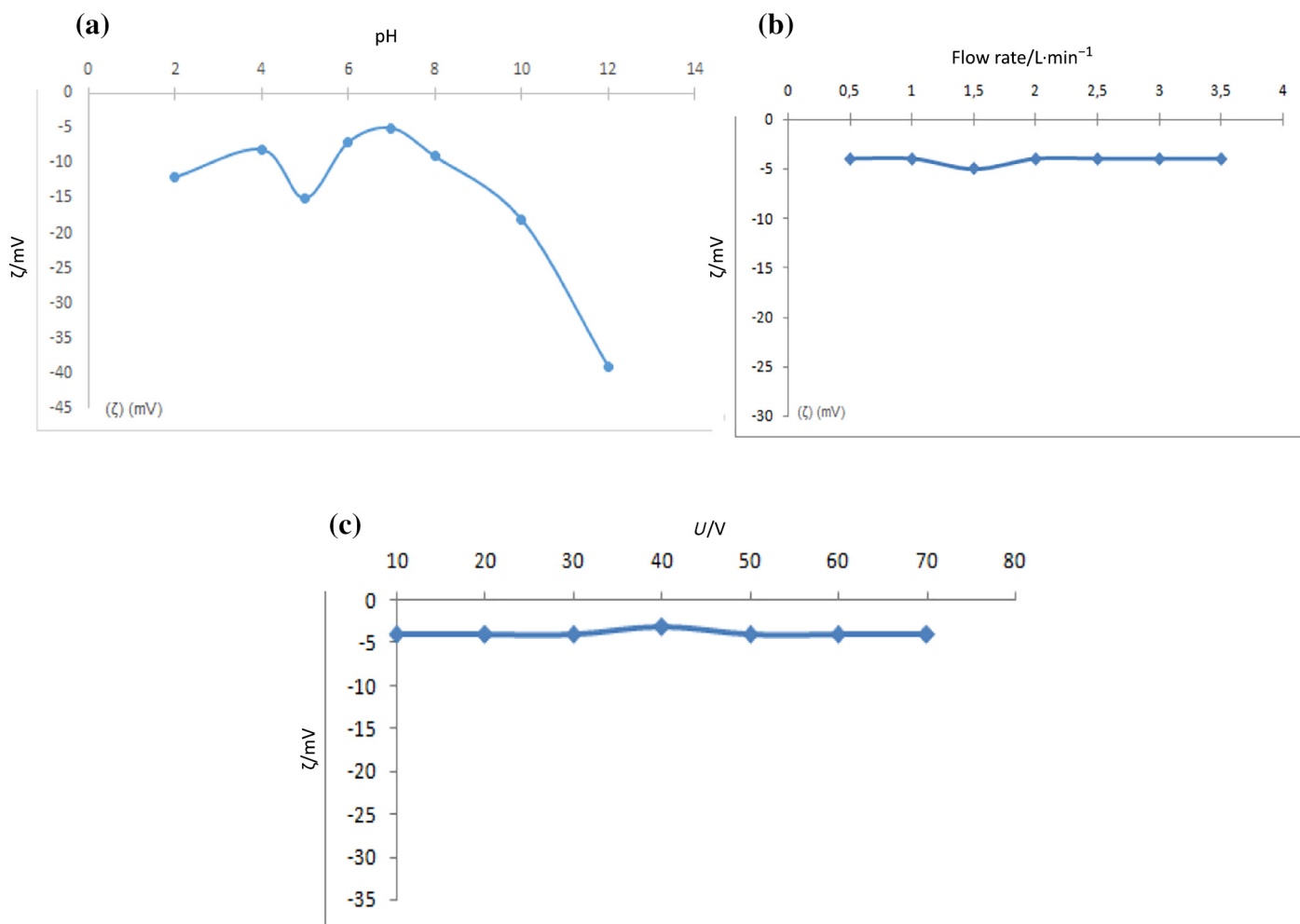


Fig. 6. Evolution of zeta potential during EC with a) pH (Voltage = 47 V, flow rate = 2 L·min⁻¹, C = 60 mg·L⁻¹); b) flow rate (pH = 7.5, voltage = 47 V, C = 60 mg·L⁻¹); c) Voltage (pH = 7.5, flow rate = 2 L·min⁻¹, C = 60 mg·L⁻¹).

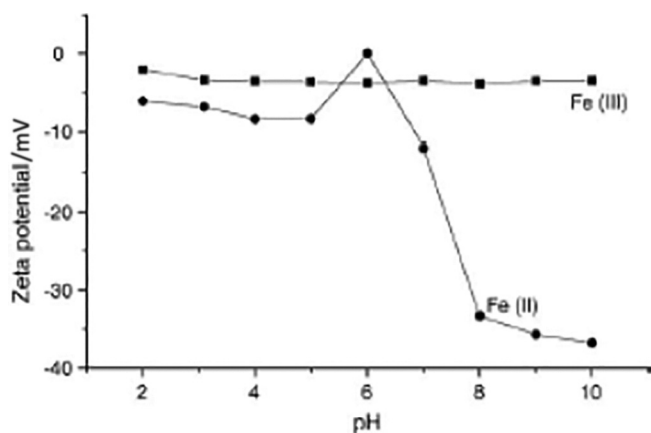


Fig. 7. Evolution of zeta potential of iron hydroxide II and III with pH resulting from iron ions synthetic solutions [61].

- The zeta potential value (-4 mV) of the effluent during EC at the optimum pH (7.5) match with the one of iron III hydroxide (Fig. 7) [61].
- The best decolorization in acidic conditions compared to the one in basic conditions could be explained by the low absolute value of zeta potential due to the presence of positives iron ions like Fe^{2+} , Fe^{3+} , FeOH^+ , FeOH^{2+} , $\text{Fe}(\text{OH})_2^+$ (Fig. 8) [62].
- The low decolorization efficiency at very high pH level ($\text{pH} > 10$) is due to the high absolute value of zeta potential related to the presence of anionic complexes ($\text{Fe}(\text{OH})_3^-$, $\text{Fe}(\text{OH})_4^{2-}$, $\text{Fe}(\text{OH})_4^-$ [62]. In fact, at

high pH level, the monomeric anions $\text{Fe}(\text{OH})_4^-$ are the major species obtained by dissolution of $\text{Fe}(\text{OH})_3$ according to Eq. (19) [40].



- At the optimum pH of 7.5, the zeta potential value remains constant (-4 mV) under different voltage and flow rate, which means that there is no change in the charge of iron precipitate. So chemical reaction between the indigo dye and the iron hydroxide ions could be excluded. The dye could be removed by van der Waals attraction and hydrogen bonding since, this kind of attraction does not change the zeta potential [61]. As reported by Sengil & Özacar [63] many species are formed during iron dissolution in water at different pH values, but the most effective species are $\text{Fe}(\text{OH})_3$ produced at pH range from 6 to 9.5. Also, according to Song *et al.* [64] and Mook *et al.* [65] the neutral pH range (from 5 to 9) was the best condition for Reactive Black 5 dye removal and the iron III hydroxide $\text{Fe}(\text{OH})_3$ adsorbs the pollutants at the surface thanks to its large surface area. Therefore, probably, the indigo dye is first neutralized and then enmeshed in porous irons III hydroxide and finally the sweep flocculation occur.

3.6. Comparison between actual and previous studies

Recently, researchers are more and more interested in CE technology and many studies have been published about this method. From literature, there is no work about blue indigo dye removal by continuous EC process. For this reason (as shown in Table 5), we compared this work with other studies which used EC technique to remove other textile dyes. However, even this work has limits. In fact, in this study

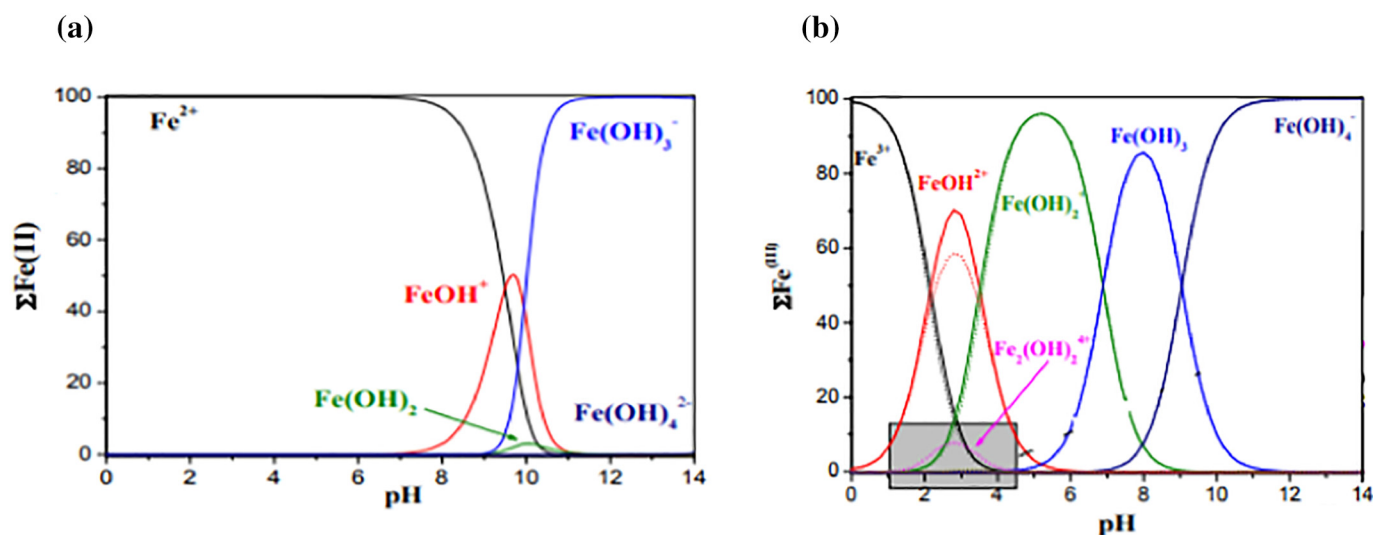


Fig. 8. Molar distribution in pure water versus pH: a) iron (II); b) iron (III) [62].

Table 5
Comparison between actual and previous studies

Used dye	Used electrodes	Method	Removal efficiency	Time/flow rate	Total cost	Reference
Blue Indigo dye	Fe/Fe	RSM	94.083%	$2 \text{ L} \cdot \text{min}^{-1}$	0.0927 USD	This study
Acid Black 172	Al/Al	RSM	90.4%	9.16 min	–	(Taheri <i>et al.</i> , 2012 [66])
Acid red 14	Fe/Fe	RSM	91.27%	4.47 min	–	(Aleboyeh <i>et al.</i> , 2008 [67])
Brilliant Green	Fe/Fe	RSM	96.1%	28 min	–	(Mariah <i>et al.</i> , 2020 [68])
Real tannery effluent	Al/Al	RSM	82.2%	–	2.92Euro	(Varank <i>et al.</i> , 2014 [69])
	Steel/Steel		67.4%		8.18 Euro	
Crystal violet	Al/Al	Individual parameters	99.75%	1 h	0.21 USD	(Ghosh <i>et al.</i> , 2008 [70])
Pretreated reel textile effluent	Al/Al	Individual parameters	90.3%–94.9%		1.5 USD	(Bener <i>et al.</i> , 2019 [71])
Methylene blue	SS/PbO ₂	Individual parameters	89.5%	180 min	–	(Othmani <i>et al.</i> , 2019 [72])
Real effluent (indigo)	Fe/Fe	RSM	95%	11 min	0.92 USD	(GilPavas <i>et al.</i> , 2020 [73])

investigation are limited to a synthetic effluent loaded with only one dye “blue indigo”. Moreover, due to some limitations, only the color removal was studied and mechanisms were established based on dye removal.

4. Conclusions

The present findings confirm that continuous electrocoagulation process with iron electrodes is a quiet effective method to remove textile dye from wastewater. The statistical ANOVA analysis and the high R^2 of 97.8% confirm the accuracy and adequacy of the developed model to predict the color removal efficiency when using the RSM technique. The optimum conditions of the process were: pH of 7.5, solution concentration of $60 \text{ mg} \cdot \text{L}^{-1}$, inlet flow rate of $2 \text{ L} \cdot \text{min}^{-1}$ and voltage of 47 V. The experimental color removal efficiency under the optimum condition was achieved at 93.97% with a total cost of $0.0927 \text{ USD} \cdot \text{m}^{-3}$. These results prove that the continuous electrocoagulation process with iron electrodes could be successfully used at industrial scale to decontaminate a real effluent with low cost and short time. The iron III hydroxides are probably the most efficient species for decolorization. The dye removal is ensured thanks to physical adsorption and flocculation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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